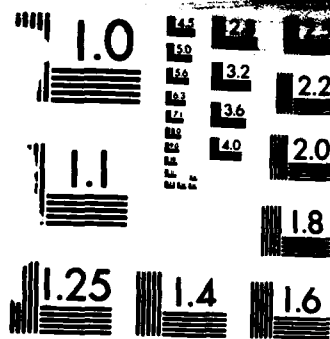


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THERMODYNAMICALLY STABLE METAL/III-V COMPOUND-SEMICONDUCTOR INTERFACES

by

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THERMODYNAMICALLY STABLE METAL / III-V  
COMPOUND-SEMICONDUCTOR INTERFACES

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ABSTRACT

Chemical reactions that occur at a metal/III-V compound-semiconductor interface should be minimized if the change in Gibbs free energy of the bulk materials with respect to any possible reaction products is positive. However, the large positive change in entropy caused by vaporization of the highly volatile group V elements is a very important contribution to the Gibbs free energy of these systems, especially at higher temperatures. Thus, a particular metal/III-V compound-semiconductor interface may be thermodynamically stable at one temperature, but unstable with respect to sublimation of elemental group V species at a higher temperature if the enthalpy change for the reaction is positive. Examination of bulk phase diagrams makes it possible to rationalize the reaction products observed and to predict which will be the most stable interface for any particular metal/III-V system.

INTRODUCTION

During the past decade, there have been an enormous number of studies of the chemistry at metal/III-V compound-semiconductor interfaces. Several workers have attempted to systematize this work by correlating chemical properties with the electrical properties of the metal/semiconductor contact; for example, the Schottky barrier height. The trend has been to look at increasingly thinner metal 'films', since the Schottky barrier height appears to be established for submonolayer coverages of metal. Because highly sophisticated instrumentation is required to study submonolayer amounts of material, the investigation of metal contacts has become a very exciting high-technology endeavor. In attempting to understand the microstructure of such systems, however, the study of macroscopic chemical properties has been almost completely ignored. This situation is probably caused by the fact that most researchers and funding agencies have little interest in the low-technology techniques used for determining phase equilibria, since not much scientific glamour or glory is associated with them.

This paper takes an alternative approach to understanding metal/III-V compound-semiconductor interfaces. The philosophy is to make certain that we understand the bulk chemistry of these contacts first. This knowledge is directly relevant to such topics as the morphology of the interfacial region and the compounds that may be found there; these in turn determine the ability to pattern extremely small features into the metallization and the reliability of a device structure. If a chemical reaction occurs at the contact interface, driven either by an anneal during the forming process or by Ohmic heating during device operation, then the geometry and electrical properties may change drastically in an uncontrollable fashion. Furthermore, establishing the bulk chemical properties of these systems will determine which materials may react with one another and what product species can be formed. With this information as a foundation, one may then examine thin film behavior to determine the relative importance of other macroscopic effects, such as bulk reaction kinetics and diffusion, as well as microscopic phenomena, such as defects and interfacial stresses and strains. Without a basic thermodynamic

In fact, the bulk thermodynamics of metal/III-V systems has not been examined very thoroughly in the past. Very little information exists for such systems regarding which phases are stable in contact with one another and which will undergo chemical reactions to form solid products. Indeed, perhaps the most common misconception is to ignore the importance of entropy in determining the reactivity of a particular metal/III-V system, even though many experiments have shown that gaseous elemental group V species are evolved at relatively low temperatures when these systems are heated [1].

## DISCUSSION

**FIG. 1 - The solidus portion of the Au-Ga-As ternary phase diagram.**

above 650 K, eutectics form between various compounds and the diagram will look significantly different. As long as the only liquid phase is nearly pure Ga, however, this diagram can be used to determine the relative amounts of different phases present in the system, given the relative amounts of the three elemental components.

Note that the boundaries of the phase diagram are defined by the three elemental components of the system at the vertices of the major equilateral triangle, which is subdivided by several *tie-lines* into smaller triangles with vertices determined by the various phases that may exist in the system. Three of those phases are elemental Au, Ga, and As.

This general topology of a ternary phase diagram at a particular temperature and pressure is required by the Gibbs phase rule [3],

$$P = C - f + 2 . \quad (1)$$

i.e., the number of phases (P) in a system is equal to the number of components (C) minus the number of specified degrees of freedom (f) plus 2. If we examine the system at a specific temperature and pressure, say 298 K and 1 atm, then  $f=2$ . Therefore,  $P=C$  and at most three phases may co-exist at equilibrium. The identity and relative amounts of each phase are determined first by using the lever rule [3] to locate the elemental composition of the system within the major triangle. Then, the lever rule may be applied again to determine the phases that are present. If the composition is specified by a point that lies on a tie-line within the major triangle, for example point A in Fig. 1, then there are only two phases, Au and GaAs, in the system at equilibrium. Tie-lines separate different three-phase regions from one another, and thus represent compositions at which an additional degree of freedom is specified; thus  $f=3$  and  $P=2$ . If, however, the composition is represented by a point such as B in the interior of a minor triangle, then there are three phases at equilibrium (GaAs, AuGa, and  $\gamma$ ). The relative amounts of the phases present are determined by using the lever rule within the subtriangle bounded by GaAs, AuGa, and  $\gamma$ , for the example of composition B. The arrangement of the tie-lines in a particular ternary system is determined either experimentally or from existing thermodynamic data [2].

Thus, the phase diagram of Fig. 1 predicts that elemental Au and GaAs form a pseudobinary system; that is, these two phases should be stable in contact with one another and do not form any interfacial compounds at any temperature. Experiments have proven, however, that chemical reactions occur with subsequent formation of intermetallic compounds of Au and Ga [4]. Are these observations of a failure of bulk thermodynamics to explain thin-film phenomena?

The ternary phase diagram in Fig. 1 is implicitly assumed to be a *closed* system; that is, there is no mass exchange between the system and its surroundings. This is true if the system is somehow encapsulated and the external pressure that is applied is greater than the vapor pressure of any volatile species. The environment in which most devices are processed or operated, however, is an open system. Thus, volatile species are either pumped away or escape into the atmosphere, which means that the actual vapor pressure of the group-V species over the solid is extremely small. The change in entropy  $\Delta S$  accompanying the sublimation of a material at pressure  $p$  compared to that at a pressure of 1 atm, the standard reference pressure for most thermodynamic systems, is

$$\Delta S = - n R \ln(p) , \quad (2)$$

where  $n$  is the number of moles that sublime and  $R$  is the gas constant.

At a particular temperature, the change in Gibbs free energy for a reaction is,

$$\Delta G = \Delta H - T \Delta S . \quad (3)$$



Even if  $\Delta H$  for a reaction involving the sublimation of a species is positive, there will always be some temperature at which the  $\Delta G$  becomes negative, since  $\Delta S$  for sublimation is positive. The size of the entropic term can be estimated by calculating  $T\Delta S$  for the sublimation of one mole of solid at a pressure of  $10^{-8}$  Torr and 298 K ( $T\Delta S \approx nRT \ln(p) \approx 62$  kJ). Thus, for Au films on GaAs heated *in vacuo*, gas-phase arsenic species have been observed to evolve at temperatures as low as 550 K [1], as predicted from simple bulk thermodynamic calculations [5]. The entropic contribution to the free energy is large enough to drive the reaction, even though it is endothermic.

The effect of this loss of As is to change the composition of the system. If a thin film of Au is deposited on a GaAs substrate, the resulting system resides on the Au-GaAs tie-line, and those are the only two stable phases at the interface. However, if the temperature of the system is raised high enough for a reaction such as



to be driven by the formation of gas-phase species ( $\text{Au}_7\text{Ga}_2$  is the approximate stoichiometry of the  $\beta$  phase), the composition of the system moves to the left on the phase diagram of Fig. 1 and the stable phases are GaAs, Au, and  $\beta$ , as observed experimentally [4]. If the process is carried out slowly, all the Au will react to form  $\beta$  phase. The next reaction will involve  $\beta$  and GaAs to form  $\gamma$  and  $\text{As}_4(g)$ , followed by  $\gamma$  and GaAs to form AuGa and  $\text{As}_4(g)$ , and finally AuGa and GaAs to form  $\text{AuGa}_2$  and  $\text{As}_4(g)$ . As long as the reactions proceed slowly, there will be at most three solid phases in the system at any given time.

Another experiment reported in this Symposium demonstrates both the thermodynamic stability of Au/GaAs interfaces and the importance of kinetics and time scale in examining solid state chemistry [6]. This TEM study did not detect any evidence of an interfacial chemical reaction for a 1000-Å film of Au deposited under ultra-high vacuum onto a freshly cleaved GaAs (110) surface, even after annealing to 400°C for 10 minutes. The failure to observe product formation after the high-temperature anneal shows that there is a kinetic barrier for the reaction. This barrier is lowered substantially for an air-exposed GaAs(110) surface, which did react strongly with an Au film. This may mean that the native oxide actually acts as a catalyst for the reaction between GaAs and Au. Thus, detailed studies of the kinetics of thin-film reactions should follow the bulk thermodynamic determinations.

This statement also applies to the study of extremely thin films. Photoemission experiments have shown that there are limited chemical reactions between Au, deposited in a monolayer-by-monolayer fashion, and GaAs (110) substrates [7]. It is possible, however, that the observed decomposition of GaAs may be assisted by the heat generated by the evaporation source, the heat of condensation of the Au onto the substrate, the electron-hole pairs generated in the substrate by absorption of visible radiation emitted by the evaporation source, or some combination of these factors. Before concluding that the observed reactions are strictly surface or interface phenomena, all other reasonable possibilities must be excluded.

Phase diagrams are also valuable as a predictive tool. For instance, if one wanted to know what the most stable Au-containing contact to GaAs is, consulting the ternary diagram in Fig. 1 reveals that it is the intermetallic compound  $\text{AuGa}_2$ . This conclusion is trivial, since there are no other Au-containing compounds (other than the liquid Ga phase with a small amount of dissolved Au) that could be a product of a reaction of GaAs and  $\text{AuGa}_2$ . Thus, a GaAs substrate with an  $\text{AuGa}_2$  film on it will be stable with respect to any possible chemical reactions until the system is heated above the non-congruent sublimation temperature, at which point the GaAs will decompose thermally.

Since any new compound containing As will be subject to thermal decomposition for the same reason that GaAs is, one may predict that, for any metallization scheme, the *most stable* metal in contact with GaAs will be the intermetallic compound that contains the *highest* percentage of Ga. This observation may also be generalized to all of the III-V compound semiconductors, and is a direct consequence of the Gibbs phase rule and the high volatility of the group-V elements.

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